

NASA TT F-14,652

by:

Translation from: Kogyo Kagaku Zasshi (Journal of Industrial Chemistry), Japanese, Vol. 71, No. 7, 1968, pp. 984-989. --

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 MARCH 1973

Unclas
G3/06 63197
RECEIVED
NASA STI FACIL
INPUT BRA
11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28

STUDIES OF THE ALKALINE POLYMERIZATION OF HYDROCYANIC

ACID AND ITS INHIBITION, PART III.

UNSTABILIZATION OF LIQUID HYDROCYANIC ACID AND STABILIZING AGENTS

[Article by Masahiro Kurabayashi and Koshin Yanagiya, Tokyo Industrial Testing Laboratory, Sixth Department, Nakameguro, Meguro-ku, Tokyo; Tokyo, Kogyo Kagaku Zasshi (Journal of Industrial Chemistry), Japanese, Vol. 71, No. 7, 1968, pp 984-989]

Abstract

With respect to the problem of instability of liquid hydrocyanic acid during storage, and the breakage of containers due to polymerization and the rapid progress of polymerization, clarification of the causes, inhibition of polymerization, and prediction of danger, we proceeded in our investigation by sealing hydrocyanic acid with stabilizing agents and other related matter in small glass ampules, maintaining them at 60°C and then observing any changes in the contents.

The results showed that first among unstabilizing reactions was hydrolysis due to moisture contained in the ampules, followed by the reaction forming the blackish-brown polymer initially at the container walls in contact with the gaseous phase (reaction promoted by oxidizing agents),

and the secondary de-ammoniation condensation of the polymers releasing ammonia gas(*2). It was found that acids with pK_a less than 3 were generally effective as stabilizing agents, particularly sulfuric acid and acids with reducing properties, and also oxy-acids which were very effective. Two or three reducing type substances used in conjunction with the acids was found to enhance the effectiveness, and that oxidant substances were actually harmful. Furthermore it was found that the progress of the de-ammoniation condensation and the accumulation of polymerization heat due to the insulating effect of the polymers were directly responsible for container breakage. Based on these results, safety measures for the storage of liquid hydrocyanic acid were studied.

1. Introduction

Hydrocyanic acid as a liquified gas tends to polymerize during storage, changing from yellow to a redish-orange color, and eventually precipitating a blackish-brown polymer, with the polymerizing proceeding so vigorously sometimes as to destroy the container. There have already been a number of studies pertaining to these characteristics of hydrocyanic acid performed from a number of different viewpoints(1)-(4), such as investigation of the unstabilization

(degradation) with long storage or heating, the accelerated progression of the polymerization reaction, the sudden rise of temperature and pressure within containers, and also the relation of moisture and other impurities to the former, but no conclusions have been obtained so far concerning the mechanism of unstabilization and the accelerated progression of the polymerization. It has been long known that acidic substances and copper powder are effective as stabilizers and they have been widely used in practice. Although Aoyama's(5) broad investigation over a long period of time, particularly on relative effects, has clarified many points, there are still many unresolved problems such as concerning acid strength, dosage, combined usage with reducing agents, and relation to the stabilizing effect.

On the assumption that this polymerization reaction is similar to the reaction forming a blackish-brown substance (azurmic acid) when an alkali is added to hydrocyanic acid, the authors investigated(6)(#2) the mechanism of the alkaline polymerization of hydrocyanic acid, and the structure and the properties of the polymer products. In the present report will be presented an analysis of the various²³ mentioned problems associated with unstabilization and polymerization resulting in container breakage, and the results of research performed to develop stabilizing agents and standards of dosage.

2. Experimental Method

2.1 Samples

With respect to the hydrocyanic acid and the tetramer, pure products described in the previous report(#2) were used, and in the case of the blackish-brown polymer, the intermediate order polymer with mean order of polymerization of 40.7 which was insoluble in ethanol but soluble in phenol was used. Mostly commercial EP grade products were used in the case of reagents, oxidants, reducing agents, formamide, and ammonium formate, but in the case of hypophosphorous acid and phosphorous acid, a calculated amount of concentrated sulfuric acid was added to the sodium salts, the freed acid then extracted with ethanol, and carefully concentrated in a platinum dish to produce a crystal(no crystal but a very viscous fluid in the case of the hypophosphorous acid), which was then considered to be 100 percent free acid. In the case of sulfur dioxide, commercial grade gas in a pressure container was used.

2.2 Ampule Storage Test

This test was conducted with pyrex ampules of about 2 ml capacity such as shown in Figure 1a, which were initially immersed for 8 hours in a chromic acid-sulfuric acid bath at 100°C, then washed with pure water, air-dried, first filled with stabilizer, other reagents and water, finally filled with 1.0 ml of anhydrous hydrocyanic acid while chilling, as much of the air replaced with nitrogen as possible, and the ampule then sealed at the end. A number of ampules

prepared in this fashion were then placed in a constant temperature air bath with double glass windows such as shown in Figure 2, the internal temperature ~~was~~ maintained at $60 \pm 1^{\circ}\text{C}$ for prolonged periods, and changes in the contents of the ampules observed through the thick glass plate. The results of observation were described by means of Aoyama's method of color tone representation(5). In comparing the results of this experiment with those performed by Aoyama, even though the same representation might have been obtained, there could be considerable difference in the progress of the polymerization due to the difference in the contents of the ampules. In order to measure the variation in temperature within the ampules during polymerization, ampules such as shown in Figure 1b with a thermocouple insert tube were prepared, and the temperature variation at roughly the center of the ampule was recorded with the differential thermocouple.

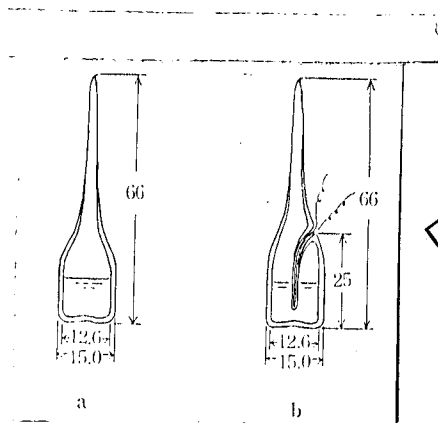


Figure 1. Glass ampules for storage test.

Figures in the diagram indicate mm.

a: For general use, b: For temperature measurement.

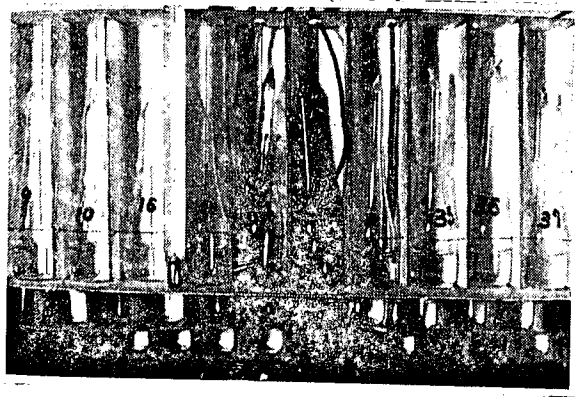


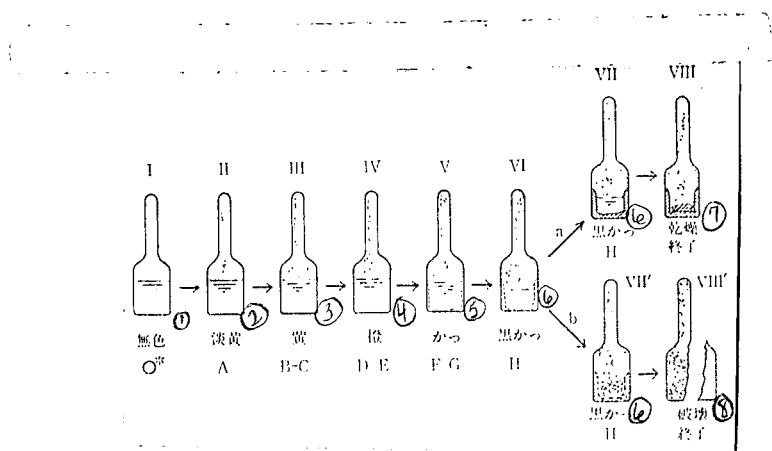
Figure 2. View of storage test.

3. Experimental Results

3.1 Outline of Storage Test

Storage tests can be roughly classified into two categories, those in which the rapid rise in internal temperature and pressure at high temperatures such as 100° - 183.5°C (critical point) over a period of hours to days is recorded (1)(2)(3), and those in which the change in content at a normal temperature of about 50°C is observed over a long period of months to years (2)(4)(8). Since we were interested in the safety aspects of storage, we chose a temperature of 60°C , which is close to normal temperature but which at the same time would produce results in a relatively short period of time. Normally test containers were hard glass containers of 100 to 200 ml capacity (2)(4), or small iron pressure vessels (1)(2)(3)(8), but glass ampules (4) were used in the present experiment to enable detailed observation of the contents. Also in order to avoid danger, the charge of hydrocyanic acid was limited to 1.0 ml (0.7 g). Since water is a common impurity to hydrocyanic acid, and since it has already been pointed out that it is related to unstabilization (1)(2)(3), the contents of the ampules were always prepared so as to contain 3 percent of water.

Although the apparent change in the contents of the ampules would vary considerably in time with the differences in stabilizers and other agents added to the ampules, generally a definite progression of events was followed, a typical progression being shown in Figure 3.



Reproduced from
best available copy.

Figure 3. Outline of progress in storage test.

a: case of inadequate moisture.

b: case of adequate moisture.

* Aoyama's color tone representation(O-H)(5).

Key: (1) Colorless. (2) Light yellow. (3) Yellow.

(4) Orange. (5) Brown. (6) Blackish-brown.

(7) Drying ended. (8) Destruction completed.

In the diagram, I shows no apparent change, and this may cover a period of days to months. II indicates a state at which the liquid starts to show color, and usually at the same time or even before, there is always the formation of a brownish solid on the wall just above the fluid level. The change from II to III is relatively slow, but the change from III through VII occurs at a rapidly accelerated pace. The change from VI to VII' to VIII' is very prominent with increasing amount of moisture, and a bulky precipitate forms not only at the bottom and along the walls, but sometimes throughout the liquid, at which time the ampule sometimes breaks. With respect to reproducibility of the experiments, it is relatively good within a batch of ampules which were all charged at the same time, but between different series, there is an error of about 10 percent. For reference in interpreting the experimental data to follow, the series of ampules charged at the same time in this test were Nos. 1-6, 7-34, 35-62, and 63-79.

When the internal temperature measuring type ampule, such as shown in Figure 1b, was charged with hydrocyanic acid containing 3 percent moisture, and stored at 60°C, there was a 19°C rise in temperature in the transition from VI to VII, as can be seen in Figure 4.

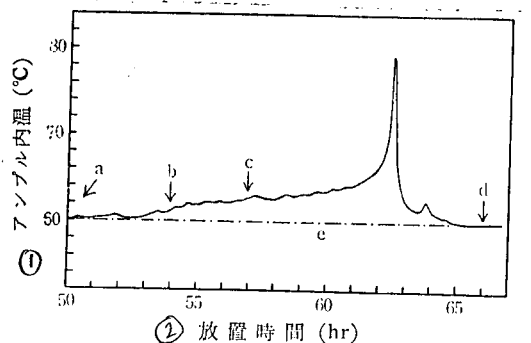


Figure 4. Rise in internal temperature of ampule due to polymerization. (H_2O 3%)

a: Precipitate adheres to internal wall(V, F).

b: Precipitate covers entire inner wall(VI, H).

c: Precipitate spreads throughout liquid(VII', H).

d: Dries out(completion).

e: Internal temperature of ampule containing isopropyl alcohol which was inserted in constant temperature bath as a compensating cell.

Key: (1) Ampule internal temperature.

(2) Storage time.

Although it was not feasible to check the contents of the ampules in storage at every stage of the change, some spot checks were made. For example, an ampule which had changed color to stage IV in Figure 3 was opened, the liquid phase evaporated, and a trace of brownish viscous substance obtained.

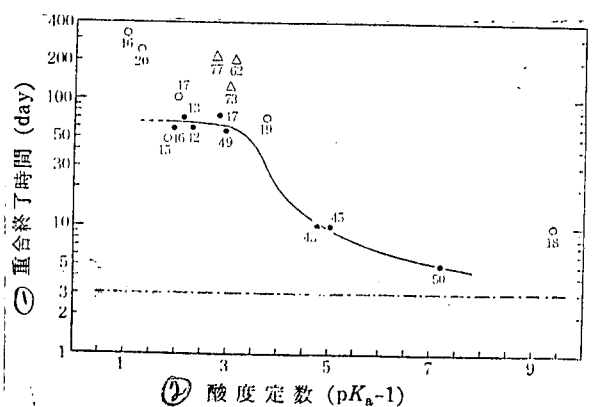
Both the evaporated matter and the residue were tested by paper chromatography(9) and the corrosive sublimate method(10) for formic acid, with negative results. Next, the ampules(VIII), in which the polymerization was completed, were broken open in a vacuum, the gases thereby generated, when analyzed by a previously reported method(*2), were found to consist of a few ml of ammonia and a small amount of carbon monoxide. The infra-red spectrum of the residual polymer was found to be identical to that of the blackish-brown polymer produced by the alkaline polymerization of hydrocyanic acid, and a minute amount(0.1 to 100 ppm of residue) of formic acid was found in the ethanol extract of the residue.

3.2 Comparison of Stabilizers

3.2.1 Acids

Although a number of acids have already been tested as stabilizers, we conducted storage tests here^{at} 60°C with some twenty readily available acids, which could be roughly grouped into four series of acids, those currently in use, those with continuously varying dissociation constants, those acids with reducing properties, and those with hydroxyl radicals. As can be seen from the results in Table 1 and Figure 5, the stabilizing effect roughly conforms to the dissociation constant in the case of weak acids, but as the dissociation constant surpasses 10^{-3} , the increase in stabilizing effect is retarded somewhat, with the effect

even decreasing to some degree in the case of strong acids such as hydrochloric acid. On the other hand, even among the strong acids, the stabilizing effect was particularly strong in the case of sulfuric acid, but low in the case of nitric acid. In contrast in the case of reducing acids, with the exception of sulfur dioxide, the stabilizing effect was better than that of the normal acids with the same dissociation constant, and in the case of hypophosphorous acid, which had the highest stabilizing capability, it had an optimum acidity of $K_a=10^{-1}$ and also reducing ability. The oxy- acids such as tartaric acid and salicylic acid were also found to have stabilizing capability somewhat superior to that of corresponding normal acids.



Reproduced from
best available copy.

Figure 5. Types of weak acids, and relation between acidity and stabilizing effect.

(H₂O 3%, acid 0.07%, 60°C)

Figures in diagram correspond to test numbers in Table 1.

●: normal acid, ○: reducing acids, △: oxy-acids,

—: no acid added.

Table 1. Storage test results(Part 1)-Comparison of acids.

No.	① 酸 類	② 酸 度 定 数 PK _a ^{b)}	③ 経 時 変 化 (day)								⑤ 重合 ^{d)} 終了
			A ^{c)}	B	C	D	E	F	G	H	
9	対 照 硫 酸	—	226	233	234	236	1		247	248	250
13	リン 酸	{ 2.148 7.198 11.75	57		64	68	69				71
15	二酸化イオ ウ	1	37	40	44	47				48	49
16	次亜リン酸	0.996	247	257	272	297		310	322	325	329
17	亜リン酸	{ 2.00 6.59	77	91	94	97	99	100			101
18	亜ヒ酸	9.4	0.17	0.4	3	4	5	6	7	8	10
19	ギ 酸	3.752	8	40	47	49	61	65	69		70
20	シュウ酸	{ 1.271 4.266	223	227	229	233	234	238	242	243	244
40	塩 酸		4	7	11	16	20	30	37	39	51
41	硝 酸		0.05		0.25	0.33	1	3	3	4	10
42	ヒ 酸	2.3	38	47		51	53	57		58	59
43	酢 酸	4.756		0.2	1		2	3	4	5	10
45	トリメチル 酢酸	5.032		0.1	0.2	0.33	1		2	2	10
46	無水マレイ ン酸	{ 1.943 6.225	45	47	51	52	54	56	57		58
47	マロン酸	{ 2.837 5.693	66	67					72	73	74
49	無水フタル 酸	{ 2.950 5.408	39	43	47	52	54			56	59
50	p-ニトロフ ェノール	7.2			0.1	0.33	1			2	5
62	クエン酸	{ 3.128 4.761 6.396	129	196	197				198	199	200
73	α-酒石酸	{ 3.036 4.360				121				121	122
77	サリチル酸	2.754	126	134	154	177	201	207	210	210	212

④ a) 各アンブルとも 3 wt% 含水シアン化水素に酸類 0.07 wt% 添加, 放置温度 60°C.
b) 特にことわらないものは 25°C の値, No.17 は 18°C, No. 77 は 30°C. 日
本化学会編, “化学便覧基礎編Ⅱ”, 丸善 (1966) p.1054.
c) アンブルの外見上の色調, 青山の表示法⁵⁾, A-H
d) 液相を認めず, 黒かっ色重合物が乾燥状態となったときを示す.

Key: (1) Type of acid.[Nos.correspond to those in table.]

9-Sulfuric acid

13-Phosphoric acid

15-Sulfur dioxide

16-Hypophosphorous acid

17-Phosphorous acid

18-Arsenous acid

19-Formic acid

20-Oxalic acid

40-Hydrochloric acid

41-Nitric acid
42-Arsenic acid
43-Acetic acid
45-Trimethyl acetate
46-Anhydrous maleic acid
47-Malonic acid
49-Anhydrous phthalic acid
50-p-nitrophenol
62-Citric acid
73- α -tartaric acid
77-Salicylic acid

(2) Acidity constant.

(3) Time lapsed.

(4) Comparison.

(5) Polymerization completed.

(6) Footnotes: (a) Each ampule contains hydrocyanic acid containing 3 wt% of water, with 0.07 wt% of acid added, storage temperature 60°C.

(b) 25°C unless otherwise noted. No.17 is 18°C, No.77 is 30°C, Reference is Kagaku Binran Kisoheii (Chemistry Handbook, Fundamentals-Vol.2), Maruzen, 1966, p.1054.

(c) Apparent color tone of ampule, following Aoyama's(5) representation, A-H.

(d) When blackish-brown polymer is dry and the liquid phase is absent.

Next in Figure 6 is shown the relation between acid dosage, the commonly used sulfuric and phosphoric acids being chosen in this case, and the days required for the completion of polymerization at 60°C.

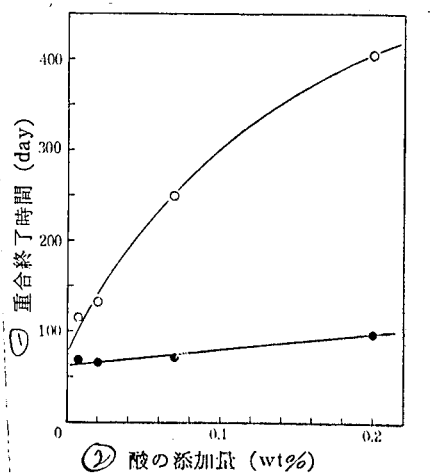


Figure 6. Relation between acid dosage and stability.
(H₂O 3%, 60°C)

●: Phosphoric acid, ○: Sulfuric acid.

Key: (1) Time for completion of polymerization.

(2) Acid dosage.

It is seen that there is a linear relationship between acid dosage and the time required for complete polymerization in the case of the phosphoric acid, but that in the case of the sulfuric acid, a higher dosage does not necessarily yield a

proportionate increase in effectiveness as a stabilizer. It is seen that the intersection of these curves with the ordinate axis is in the vicinity of 60 to 80 days, which corresponds roughly to the time it takes hydrocyanic acid, containing 3 percent moisture, to polymerize completely. In comparison, the small value of three days given for the comparison test (no additive) in Table 1 is probably due to some alkali dissolving out from the seal section of the ampule and accelerating the polymerization reaction.

3.2.2 Influence of Oxidizing and Reducing Agents on the Stabilizing Effect of Acids

Concentrating on the fact that acids with reducing properties have a superior stabilizing effect, several substances with oxidizing or reducing characteristics were chosen for testing, with 0.5 wt% of these substances being added to the hydrocyanic acid which had already been stabilized with 0.07 wt% of phosphoric acid. These samples were subjected to the storage test, and the combined effect of the additive and the acid were studied.

According to Table 2, benzoyl peroxide, which is known to be one of the active agents for starting polymerization by radical polymerization, suppresses the stabilizing effect, but α, α' -azobisisobutyronitrile, which is known to have softer action, hardly has any effect.

Table 2. Storage test(Part 1)- Effect of oxidizing and reducing agents.

No.	添 加 物 ⁽¹⁾	経 時 変 化 (day) ⁽²⁾								重 合 終 了 ⁽³⁾
		A	B	C	D	E	F	G	H	
13	—	57		64	68	69				71
34	過酸化ベンゾイル	4		5	7	10	12	27	28	30
54	α, α' -アゾビスイソブチロニトリル	40	51	53	59	60	62			64
33	p-ベンゾキノン					61	63		64	65
29	ヒドロキノン	77	85	89	90		91			93
32	イオウ粉	75	85	115	117		119	120	121	129
30	ホルムアルデヒド	61	64	65	66	76				81
52	パラアルデヒド	45	51	53	73	79	84	88		89
53	ベンズアルデヒド	43	44	48	67	73	112	125		128

⁽⁴⁾a) 水 3.0 wt%, リン酸 0.07 wt%, 60°C.
 b) 0.5 wt% 添加.

Key: (1) Additive[keyed to Nos. in table.]

13-.....

34-Benzoyl peroxide

54- α, α' -azobisisobutyronitrile

33-p-benzoquinone

29-hydroquinone

32-sulfur powder

30-formaldehyde

52-paraldehyde

53-benzaldehyde

(2) Time lapsed.

(3) Completion of polymerization.

(4) Footnotes: (a) Water 3.0 wt%, phosphoric acid 0.07 wt%, 60°C.

(b) 0.5 wt% added.

On the other hand, Hydroquinone, which belongs to a group of relatively powerful suppressors, and sulfur powder (which effect was discovered by Onoda) (4) both enhance the stabilizing effect of the phosphoric acid. Among others, the aldehydes seem to have some multiplying effect in conjunction with the phosphoric acid, the benzaldehyde having the clearest effect. These reducing substances also tend to extend the time of complete polymerization measured from the time coloration is first observed.

3.2.3 Heavy Metal Powder

In Table 3 are shown the results of testing in which 1 wt% of four different heavy metal powders were added to the hydrocyanic acid containing 3 wt% of moisture. The fact that iron and tin powder have no stabilizing effect, but that copper and zinc powder are effective agrees with the experimental results obtained by Aoyama (5) and Hatano et al (11).

Table 3. Storage test (Part 3) - Effect of heavy metals.

No.	金属粉 ^①	② 経時変化 (day)								③ 追合終了
		A	B	C	D	E	F	G	H	
21	銅	121	128	130						131
22	亜鉛	40	41	42						43
23	鉄	0.25	1	4	5	5	6	7	8	10
24	スズ	0.2	0.4	3	3	4	4	5	5	10

④ a) 水 3.0 wt%, 金属粉 1.0 wt%, 60°C

Key: (1) Heavy metal powder [Nos. correspond to those in table.]

21-Copper

22-Zinc

23-Iron

24-Tin

- (2) Time lapsed.
- (3) Completion of polymerization.
- (4) Footnotes: (a) Water 3.0 wt%, metal powder 1.0 wt%, 60°C.

3.2.4 Heavy Metal Salts

In Table 4 are shown the results of adding four different heavy metal chlorides at the rate of 0.2 wt%. As already pointed out by Aoyama(5) and Hatano(11), these salts have a considerable stabilizing effect, the zinc chloride being particularly superior. Also with the addition of such a small amount as 0.2 wt%, most of the salt in each of the cases dissolved in the hydrocyanic acid with only a slight noticeable precipitate.

Table 4. Storage test(Part 4)-Effect of heavy metal salts.

No.	① 金属塩	② 経時変化 (day)								③ 重量%
		A	B	C	D	E	F	G	H	
25	塩化第二銅		57	61	63	65	75	76	77	79
26	塩化亜鉛	100	—	— ^{b)}	202	203	204	208		209
27	塩化第二鉄		84	85	91	94				97
28	塩化ニッケル	89	90	91	93	99	100			103

④ a) 水 3.0 wt%, 金属塩 0.2 wt% 添加, 60°C.
b) この間数回無色にもどる.

Key: (1) Metal salt[Nos.correspond to those in table.]

25-Cupric chloride

26-Zinc chloride

27-Ferric chloride

28-Nickel chloride

(2) Time lapsed.

(3) Completion of polymerization.

(4) Footnotes: (a) Water 3.0 wt%, metal salt 0.2 wt%,
60°C.

(b) Color vanishes several times in this interval.

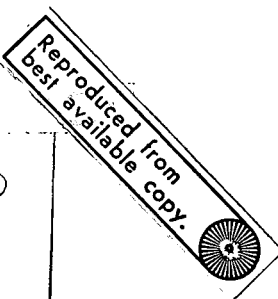
3.3 Effect of Hydrocyanic Acid Related Substances on Destabilization

Substances which could easily coexist or which might have the probability of existing with liquid hydrocyanic acid in storage would include in addition to water, the hydrolyzed products of hydrocyanic acid such as formamide or ammonium formate, the alkaline polymerized products such as the tetramer and the blackish-brown polymer, and in Table 5 are shown the results of storage test at 60°C with small amounts of these related substances added to the hydrocyanic acid which has already been stabilized by phosphoric acid. It is seen that all of these substances tend to reduce the stabilizing effect of the phosphoric acid, the blackish-brown polymer particularly having a strong action, followed by ammonium formate, while the actions of formamide and the tetramer are fairly weak.

Table 5. Storage test(Part 5)-Effect of hydrocyanic acid related substances.

No.	添加物 (wt%) ①	② 経時変化 (day)								重合終了 ③
		A	B	C	D	E	F	G	H	
13	—	57		64	68	69				71
55	ホルムアミド 0.25	32	37	41	43	47	48		51	52
56	ホルムアミド 0.50	13	17		23	28	32	35	37	38
57	ギ酸アンモニウム 0.25	0.2	0.3	1	1	3	4	11	13	16
58	ギ酸アンモニウム 0.50	0.2	1	1	2	4	7	13		17
59	四量体 0.50	0	2	7		37			38	39
60	黒かっ色重合物0.25	—	—	—	—	0		1	2	5
61	黒かっ色重合物0.50	—	—	—	—	0	0.2		1	3

④^a 水 3.0 wt%, リン酸 0.07 wt%, 60°C.



Key: (1) Additive[Nos.correspond to those in table.]

13.....

55-Formamide

56-Formamide

57-Ammonium formate

58-Ammonium formate

59-Tetramer

60-Blackish-brown polymer

61-Blackish-brown polymer

(2) Time lapsed.

(3) Completion of polymerization.

(4) Footnote: (a) Water 3.0 wt%, phosphoric acid 0.07 wt%, 60°C.

3.4 Effect of Hydrogen Peroxide and Other Substances on Hydrocyanic Acid

Since it was found that benzoyl peroxide hindered the stabilizing action of acid, the experiment shown in Figure 7 was performed to see whether peroxides had any direct action on hydrocyanic acid or not. In the diagram, a small pyrex glass container holds 1.0 ml of hydrocyanic acid and a small amount of the peroxide, the flask being immersed in a 30°C constant temperature bath, and changes in the content of the flask were observed with the circulating cooling device attached.

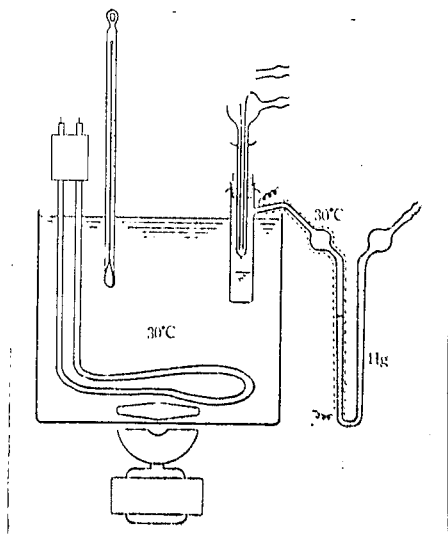
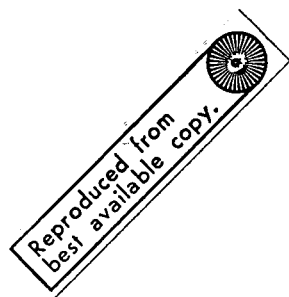


Figure 7. Device for reaction of small amounts of hydrocyanic acid.

As can be seen from the results in Table 6, hydrogen peroxide has a strong action on polymerization of hydrocyanic acid, particularly in the gaseous phase or on the container walls in contact with the gaseous phase. In contrast, benzoyl peroxide had no polymerization action inside of 28 hours.

Table 6. Action of peroxides on hydrocyanic acid.

No.	① 水 (wt%)	② 過酸化物 (wt%)	③ 経過変化 (hr)	④ 着色発見	⑤ 黒沈発見	⑥ 備考
U-1	4.1	—	—	2hr	274	—
U-7	1	過酸化水素 ⑩ 0.43	—	—	4~7	器壁の露出部に褐色固形物を多量に生成し、液相は無色 (7)
U-8	—	過酸化ベンゾイル ⑪ 0.71	—	—	—	20 hr で実験中止 (8)
U-9	1.0	過酸化ベンゾイル ⑪ 1.14	—	—	—	28 hr で実験中止 (9)
a) ② 浴温 30℃, 沸点処理.						



Key: (1) Water.

(2) Peroxide.

(3) Time lapse.

(4) Coloration discovered.

(5) Black precipitate discovered.

(6) Remarks.

(7) Brown solid produced profusely on exposed walls of container, while liquid phase is colorless.

(8) Experiment terminated at 20 hours.

(9) Experiment terminated at 28 hours.

(10) Hydrogen peroxide.

(11) Benzoyl peroxide.

(12) Footnote: (a) Bath temperature 30°C, boiling point treatment.

3.5 Action of Ultraviolet Rays

A quartz glass ampule of about 1.5 ml capacity was roughly half-filled with anhydrous hydrocyanic acid, sealed, and then exposed to intermittent radiation from a Tokyo Shibaura make mercury lamp, type SHL-100 UV, brightness 1500 cd/cm^2 , at a distance from the light source of 14 cm. The test showed that coloration was observed after 23 hours of irradiation, and the black precipitate was formed after 223 hours. Upon allowing the ampule to stand at room temperature without irradiation, the polymerization was observed to progress, attaining complete polymerization after about a month.

4. Discussion

The principal reaction occurring in the polymerization of standing anhydrous hydrocyanic acid is almost definitely alkaline anion polymerization, based on the nature of the products which are formed in the polymerization. There must therefore exist some destabilizing reaction, prior to occurrence of the polymerization, which tends to make the hydrocyanic acid alkaline.

In the standing storage tests, a blackish-brown polymer has been observed to form on the container walls above the liquid level once the stable period has past, and generally coloration of the liquid phase arises from this formation being washed down from the walls by the condensate of hydrocyanic acid. On one hand, the stable period of hydrocyanic acid,

which has been acid stabilized, is shortened by the addition of benzoyl peroxide, but extended by the addition of reducing agents such as hydroquinone, the aldehydes, or sulfur powder(*5). Also noting that the addition of hydrogen peroxide rapidly produces a blackish-brown solid on the wall at the liquid line(*6), all this evidence suggests that some form of oxidation reaction related to the destabilization(*7) must be occurring in the gaseous phase or at the walls.

That the blackish-brown polymer generates destabilization has been proven by Gause et al (3) and Onoda(4), and our standing storage tests have also indicated that this substance acts strongly to shorten the stable period, more than any other related substance. This blackish-brown polymer tends to emit ammonia and a faint smell of hydrocyanic acid in air(13), and Onoda has shown that the addition of this substance will shift the hydrocyanic acid towards the alkaline(4). We have further shown in a previous report(*2) that the relatively low order blackish-brown polymers readily emit ammonia and hydrocyanic acid upon heating or by the action of water vapor, and that further condensation takes place.

The above evidence seems to show that the blackish-brown polymer promotes the polymerization of hydrocyanic acid through the secondary de-ammoniation condensation of

of the polymer. The fact that the tetramer has a weaker action than the blackish-brown polymer in promoting polymerization agrees with the fact that the tetramer has a stable conjugate structure which does not lend itself easily to de-ammoniation condensation.

According to Figure 6, there is a linear relation between the dosage of phosphoric acid and the days required for complete polymerization, but in the case of sulfuric acid, the curve takes a downward trend. The latter phenomenon can probably be attributed to the fact that further addition of a strong acid such as sulfuric acid only promotes the production of more ammonium formate through hydrolysis. It is known(14) that hydrochloric acid has a stronger hydrolytic action than sulfuric acid on hydrocyanic acid, and the results of a standing test have also shown that hydrochloric acid has less of a stabilizing effect(#8). It was originally assumed that the hydrolysis of hydrocyanic acid was the primary cause of a destabilizing reaction, but from the evidence obtained in this study, polymerization reactions at the container walls now seem to outweigh hydrolysis as the main source of destabilization. Favorable evidence includes the fact that formamide and ammonium formate, which are products of hydrolysis, promote polymerization less than the blackish-brown polymer, also the fact that no ammonium formate was discovered in the ampules which had started to color in the standing storage tests, and also the fact that

when a small amount of polymer was formed by the ultraviolet irradiation of anhydrous hydrocyanic acid, no further irradiation was necessary for the polymerization to continue. There has been some consideration of the existence of the isonitrile form of hydrocyanic acid to either start the polymerization reaction or to at least be the cause of destabilization(13)(4), and there could be some relation to the previously described wall reaction, however, we did not pursue this line of investigation.

Once coloration of the liquid phase in the ampules is observed, the coloring thereafter deepens at an ever increasing pace, which is subsequently followed by the precipitation of polymers, and the production of the precipitates is also rapidly accelerated. It was observed in the first report(6) that the degree of coloration for several hours following addition of an alkali to the hydrocyanic acid increased proportional to the time, during which period the alkalinity of the solution also remained constant. The apparent discrepancy between this and the standing ampule tests is only the result of a great difference in time scales of the two experiments, that is, the coloration speed in the first report only represents the polymerization speed at a single time point in the standing ampule tests.

With respect to the rise in internal temperature and possible destruction of the ampules in the standing storage test, considering the fact that neither the polymers nor the hydrocyanic acid is explosive, also that the gas emitted during polymerization is inadequate to account for internal pressure rise as proven by Aoyama(2), the heat of polymerization remains the only factor to be considered. Gause et al(3) have obtained a value of 10.2 kcal/mol for the heat of polymerization under conditions of very slow polymerization upon adding an alkali, and we should also include the heat of secondary de-ammoniation condensation, which was previously reported(*2). The mechanism for ultimate accumulation of this heat of polymerization must include, in addition to the rapidly increasing alkalinity resulting from the de-ammoniation condensation, the heat insulating and convection suppression effects resulting from the formation of bulky polymer products. The bulkiness of the polymers is particularly intimately related to the water content, and this will be discussed in detail in a later report.

Acids are the most suitable stabilizing agents since they extend the period to coloration of the hydrocyanic acid enormously, but it should be noted that a parallel relation exists between the stabilizing effect in the case of weak acids and the acidity in water solution.

Although this is to be expected from the work by Hatano et al(11), who determined a parallel relationship between the acidity, the electrical conductivity in hydrocyanic acid, and pH reducing action for several types of acids, the standing ampule tests also show that additives such as p-nitrophenol which has an acidity constant(pK_a) almost the same as that of hydrocyanic acid has almost no stabilizing effect. Such an effect has been clearly observed only for additives with pK_a less than 5, with a very definite effect when pK_a was less than 3.

The results of the standing tests have shown that sulfuric acid and phosphoric acid, which are both in current use as stabilizers, both have sufficient stabilizing effect, and that furthermore oxalic acid, hypophosphorous acid, and phosphorous acid, which have appropriate pK_a values and also a reducing action, would make ideal stabilizing agents. With respect to the use of a combination of an acid and a reducing agent, the use of sulfur dioxide with sulfuric acid or phosphoric acid, or of sulfur powder with maleic acid has been recommended(4), and the efficiency of using in combination with a few other reducing substances such as benzaldehyde has also been noted. The oxy-acids, tartaric acid, citric acid, and salicylic acid, similar to the reducing acids, have been found to have a stronger stabilizing effect than what might be expected from the value of pK_a alone.

The reason for this is not clear, but considering the fact that these acids are only weakly corrosive to metals, special uses might be found. With respect to acid dosage, favorable results have been reported for dosages in the range of 0.005 to 3 wt%, however, our studies show that there is considerable effect even for small dosages such as 0.007 wt%, such that the required objective can be achieved actually with a very small quantity. In practice, the selection of a suitable stabilizer and proper dosage must be judged by the length of intended storage, the hazards of contamination by alkalis or polymers, the degree of safety management desired, corrosion problems, and the effect on the end use of the hydrocyanic acid, as well as other factors.

With respect to the effect of heavy metals, Hatano et al have shown that effective metals such as copper, silver, zinc, and nickel reduce the pH of the hydrocyanic acid and increase its electrical conductivity, but further details are unknown, except that it can be surmised that either the metal or some compound of the metal at the surface probably dissolves into the hydrocyanic acid to produce the stabilizing effect.

With respect to the effect of the salts of heavy metals, the stabilizing effect is probably due to the proton released by the formation of cyanacetate in the hydrocyanic acid, as pointed out by Jander(15).

Aoyama has reported that the halogen compounds of arsenic, tetralin, and tin maintain their stabilizing effect for a number of years, but there has been no follow-up testing of these results.

With respect to the different types of stabilizers available, there is no need to select a special agent unless the storage is to be for an extended period, and generally the selection is based on factors such as the effect on the intended use of the hydrocyanic acid, or the corrosion of apparatus.

In conclusion it should be noted that since ampules were used in the present experiment, the effect of glass cannot be neglected. It should also be noted that there was a large difference in temperature between room temperature and the 60°C used in the experiment, and that a number of problems probably remain to be resolved before the results of these experiments can be applied to practice. However, from the standpoint of phenomena which would be most significant to safety measures for the storage of liquified hydrocyanic acid, the following could be given: the addition of stabilizing agents, pH(*9), coloration(*10), periodic check of stabilizer consumption(*11), internal temperature of container, installation of device warning

of internal pressure rise, training for the emergency blending or unloading of stabilizing agents, reduction of storage temperature, the avoidance of complex-shaped containers, the cleaning of containers before charging, and other matters.

(Presented at Sixth Disaster Prevention Seminar, January 1965.)

The authors thank Y.Ando of this laboratory for his many helpful suggestions during the course of this study.

BIBLIOGRAPHY

- (*2) Previous report(Second Report), Kurabayashi, M., Yanagiya, K., Yasumoto, Y., and Kamakura, T., Kogyo Kagaku Zasshi(Journal of Industrial Chemistry), Vol.70, 1106(1967).
- (1) Walter, M., and Eldred, D., Ind.Eng.Chem., Vol.17, 1074(1925).
- (2) Aoyama, T., High Pressure Gas, Japanese, Vol.18, 167, 207(1954).
- (3) Gause, E., and Montgomery, P., J.Chem.Eng.Data, Vol.5, 351(1960).
- (4) Onoda, K., Agricultural Chemistry, Japanese, Vol.36, 575(1962).

- (5) Aoyama, T., High Pressure Gas, Japanese, Vol.19, 121, 176, 209(1955).
- (6) Kurabayashi, M., Yanagiya, K., and Kamakura, T., J.Ind.Chem., Japanese, Vol.70, 352(1967).
- (7) Abegg, R., Handbuch der Anorg.Chem., III, 3, S.Hirzel, Leipzig(1907), p.426.
- (*4) Because of this, the experimental results contain the effects of leaching of alkali from the glass or of some alkaline effect at the surface of the glass.
- (8) Walker, M., U.S.P.2194370(1940).
- (9) Mukerjee, H., Anal.Chem., Vol.31, 1284(1959).
- (10) Auerbach, F., and Plüddemann, W., Chem.Zentral.Blatte., 688(1909).
- (11) Hatano, T., Ando, Y., Nakanouchi, H., Abstracts of 10th Meeting, Japan Chemical Society, 303(1957); Kurabayashi, M., and Ando, Y., Kagaku Kogyo Shiryo (Chemical Industry Data), Vol.32, 104(1965).
- (*5) The reducing agents only enhance the stabilizing effect of the acids, having no stabilizing action of their own.
- (*6) Hydrogen peroxide is known(12) to dissociate hydrocyanic acid into ammonia and carbon dioxide, and if this ammonia is the cause, then polymerization will progress even in the liquid phase.

- (*7) Even though this may belong the category of polymerization starting or stopping agents in the case of socalled radical polymerization, there may be no effect during the stable period.
- (12) Beilsteins Handbuch, Bd.2-1(1929), p.24.
- (13) Völker, V., Angew.Chem., Vol.69, 728(1957).
- (*8) It is even lower because of the oxidation action of nitric acid.
- (14) Migridichian, V., Chem.Org.Cyanogen.Comp., Reinhold Publ. Corp., New York(1947), p.38.
- (15) Jander, G., Z.Physik.Chem., A, Vol.192, 167(1943).
- (*9) With acid additive, there is danger when indication with a glass electrode pH meter exceeds 2.
- (*10) Because of the low solubility of the polymers in hydrocyanic acid, the color tone will be no darker than about D when the precipitate has been removed.
- (*11) There is a method of checking by titration(16) in the case of acid additive.
- (16) Aero HCN Bulk Handling, Am.Cyanamid Co., U.S.A., p.30.

5576

CSO: R- 15782-D